Evaluating Thallium Leaching from Fly Ash in Aquatic Systems

Honors Research Thesis

Presented in Partial Fulfillment of the Requirements for the Bachelor's of Science with Honors Research Distinction

Lauren Czaplicki
The Ohio State University
2012

Thesis Committee
Harold Walker PhD.
John Lenhart PhD.

Abstract

To develop a fundamental understanding of how water chemistry and the physical and chemical properties of fly ash influence the release of thallium in natural and engineered aquatic systems I used leaching tests, graphite furnace atomic absorption spectroscopy, and the synchrotron generated x-rays of very high energy at Argonne National Laboratory. I evaluated and characterized the leaching of thallium as a function of pH, liquid to solids ratio (L:S), and ash origin. To complement the leaching data, specific molecular-level details describing thallium with speciation in fly ash acquired from various coal combustion power plants were collected via x-ray absorption spectroscopy (XAS). This work gives information on the intrinsic leaching behavior of different ashes. This has the potential to be used to project long term cumulative release of Tl from fly ashes under various management scenarios.

The determination of the exact speciation of Tl in fly ash will help to explain and predict the leaching behavior of thallium in fly ash ponds and other aquatic systems in the built and natural environments. Results from leaching tests in which the effect of varying liquid to solid ratios on leaching behavior is examined indicate as the L:S increased, the amount of thallium leached logarithmically decreased. This suggests a more complex leaching mechanism than dilution is at play, as an isolated dilution process would result in a linearly decreasing variance. These results suggest the existence of multiple species of thallium, of varying accessibility and solubility, but literature examining this possibility in fly ash is scarce. XAS analysis showed multiple species of thallium present in each ash. This knowledge of the specific thallium speciation in fly ash within aquatic systems is extremely valuable. Specific information derived from XANES helps to evaluate whether Tl speciation and leaching is dependent on pH conditions, L:S ratio, and source coal.

Acknowledgments

I thank Dr. Hal Walker, for guidance, encouragement, and support of my scientific curiosity. I am grateful to Dr. John Lenhart for sharing his expertise and experience with XAFS/XANES and making it possible for me to experiment using the synchrotron. I also thank Dr. Jason Cheng and Mengling Stuckman for their explanations and help with interpreting the XANES data. I also wish to thank Quing Ma, beamline scientist at Argonne National Laboratory for his assistance in gathering the APS data.

Contents

List of Figures 6
List of Tables 6
Introduction 7
Source Background 7
Thallium Concern Background 9
Previous Work 10
Significance 10
Experimental Methodology 11
Overview of method options 11
pH Evaluation Method 12
Variable Liquid to Solid Ratio Evaluation Method 15
Graphite Furnace Atomic Absorption Spectroscopy Total Thallium Measurement Method 16
Synchrotron Test Method 18
Results & Discussion 21
Data Treatment 21
pH Test Results 21
L:S Test Results 25
Synchrotron Results 28
Analysis 32
pH Result Analysis 32
L:S Result Analysis 33
XANES Analysis 34
Conclusions & Future Directions 35
Bibliography 36
Appendix A: Calibration Data 37
Calibration Standards & Curve 38
Appendix B: Total Thallium Analysis Data 39
Raw Data with Quality Control Checks 40
Metadata from Final Analysis 41
Compiled Data 42

List of Figures

Figure 1:An aerial photo of a fly ash pond (EPRI)..... 8
Figure 2: Rotating Pre Method 1313 Samples 13
Figure 3: Vessels used for method 1313 14
Figure 4: Schematic of graphite furnace apparatus (Slavin) 16
Figure 5: Cross section of a thallium hollow-cathode lamp (Slavin) 17
Figure 6: GFAAS 17
Figure 7:DND CAT beamline 18
Figure 8: Sample placement across from fluorescence detectors in ionization chamber 19
Figure 9: meq additions of acid and base have an impact on total thallium concentration leached..... 22
Figure 10: pH influence on total thallium concentration released during leaching..... 23
Figure 11: Normalized pH driven thallium release during leaching as a function of pH..... 24
Figure 12: Preliminary L:S results, filtered through .45 micron filter and acidified with 2%HNO3 ... 25
Figure 13: L:S ratio effect on total thallium concentration leached into solution 26
Figure 14: Variable L:S ratio driven thallium release by each gram of fly ash over the leaching period 27
Figure 15: Scan of Primary fly ash without any treatment with various additions 28
Figure 16: First derivative of Cardinal fly ash scan without any treatment with various additions..... 29
Figure 17: Scan of Various Ashes compared with various standard additions 29
Figure 18: First derivative of Various Ashes compared with various standard additions..... 30
Figure 19: Scan of several different treatments of Cardinal fly ash compared with various standard additions..... 30
Figure 20: First derivative of several different treatments of Cardinal fly ash compared with various standard additions 31
Figure 21: Approximate speciation of various fly ashes and various treatments to Primary fly ash ... 31

List of Tables

Table 1: Relative elemental composition of ash (EPRI) 7
Table 2: Pre method addition schedule & resulting pH values 13
Table 3: Method 1313 addition schedule 15
Table 4: SR003.1 additions 15
Table 5: Values and quality control checks of preliminary L:S results..... 25

Introduction

Source Background

Coal combustion produces fly ash, which is mainly composed of silicon, aluminum, iron, and calcium with trace amounts of thallium and other metals (Maryland Department of Health). "Thallium volatizes during the burning of coal and recondenses on the surface of ash particles … These particles contain up to 50 mg thallium per kg fly ash" (International Programme on Chemical Safety). The general composition of fly ash varies but tabulated below in Table 1 is relative elemental composition of ash from a traditional cyclone boiler fed with bituminous coal and a circulating fluidized bed combustion (CFBC) boiler fed with bituminous coal with limestone addition for sulfur removal.

Table 1: Relative elemental composition of ash (EPRI)

Element	Oxide	Cyclone Boiler Relative Composition (% by weight)	CFBC Relative Composition (% by weight)
Silicon	SiO_2	37.30	16.53
Iron	Fe_2O_3	32.70	23.99
Aluminum	Al_2O_3	19.00	6.03
Calcium	CaO	1.98	40.25
Chlorine	ClO_2	.04	Not Analyzed
Magnesium	MgO	0.94	0.48
Phosphorus	P_2O_5	0.31	0.00
Potassium	K_2O	4.03	1.18
Sodium	Na_2O	0.63	0.24
Sulfur	SO_3	1.75	10.96
Titanium	TiO_2	1.33	0.33

The majority of fly ash is disposed of in landfills or in open air fly ash ponds as seen in Figure 1. In 2007, United States coal-fired power plants produced 72 million tons of fly ash

(EPRI). There is significant concern over groundwater and surface water contamination, since the threshold limit for thallium in drinking water is 0.002 mg/L (U.S. E.P.A.).

Figure 1:An aerial photo of a fly ash pond (EPRI)

Fly ash ponds have garnered public concern as recently as 2008, when 5.4 million cubic yards of coal ash spilled into the area around the Kingston Fossil Plant in Harriman, Tennessee as a result of a retaining wall failure. The spill was enough to flood more than 3000 acres one foot deep. Tests of nearby river water resulted in elevated levels of thallium and lead. **(Dewan)**

Several fly ashes have been obtained from among the largest electric power plants in Ohio for this research. Fly ash composition is largely dependent upon the fuel source. Bituminous, subbituminous, lignite, and low-BTU coal will have different compositions, as will cyclone, tangential, frontfired and circulating fluidized bed combustion boilers result in different fly

ashes. Also, the presence of Selective Catalytic Reduction (SCR) equipment to remove NO_x and/or FGD scrubbers to remove SO_x from flue gases will also influence this composition. The natural pH of the fly ash slurry also depends on the source. Low-sulfur coal from the west can result in pH ranges from 8 to 12, while bituminous coal from the east has a pH near 4 (EPRI). Thus, to assure consistency throughout this project, I have worked with mainly one type C fly ash of bituminous coal origin.

Thallium Concern Background

Potential health effects from long-term exposure to thallium at levels greater than the threshold include kidney, intestine or liver problems (Maryland Department of Health) (U.S. E.P.A.). Short term thallium exposure above 2 ppb causes gastrointestinal irritation and nerve damage, while long term exposure to levels over 2 ppb can cause changes in blood chemistry, hair loss, and liver, kidney, intestinal, and testicular damage (U. S. Environmental Protection Agency). The Environmental Protection Agency believes that all potential health problems would be avoided for thallium levels below 0.5 parts per billion in a liquid matrix.

The behavior of thallium in the environment is not well understood, nor do methods exist to control the effluent levels of thallium. Many parameters may influence thallium states in the environment. Metals in coal combustion products (CCPs) have been studied before, though thallium is in need of further study. "The thallium in fly ash most likely resides as an oxide or in the nonvolatilized sulfide fraction. Thallium leaching from CCPs may be a result of mineral solubility or cation exchange with ammonium, an issue that calls for further research" according to EPRI (EPRI). Power generation facilities can control the liquid to solids ratio (L:S) and the pH of their fly ash ponds. This research focuses on understanding the relationship between these variables and thallium release in the mobile aqueous phase in fly ash pond systems.

Previous Work

Work has been done to examine the leaching of other heavy metals like selenium, arsenic, and vanadium from fly ash. Thallium has not been studied in this manner before, however and little is known about thallium mobility in groundwater and surface water. Thallium is a transition state element with +1 and +3 valence states. Thallium exists mainly as thallium Tl(+1) in natural waters. A few studies on thallium in groundwater suggest that it is relatively immobile under typical pH conditions and increases in mobility under acidic conditions (EPRI). Currently, the U.S. EPA's best demonstrated available technology to remediate thallium involves chemical oxidation followed by precipitation via hydroxide compound formation, settling, and filtration (EPRI).

This work takes a three part approach to evaluating the fly ash leaching of thallium: leaching under variable liquid to solid ratios, leaching under variable pH conditions, and x-ray absorption spectroscopy of various fly ashes for thallium speciation. The analysis method used to measure total thallium resulting from the variable liquid to solid ratios and variable pH conditions is well accepted by the specialists in coal combustion byproduct quantification. Furthermore, methods used to identify speciation in thallium are similar to methods used in identifying selenium and vanadium via x-ray absorption fine-structure spectroscopy (XAFS), specifically x-ray absorption near-edge spectroscopy (XANES) (Kirk G Scheckel). The Kosson Integrated Framework is currently being integrated into the US EPA standard methods and is a guide for the pH variable and liquid to solid ratio variable tests.

Significance

Understanding the thallium leaching behavior of different fly ash samples under varying solution conditions is important to better conceptualize thallium release. Moreover, thallium

transport and toxicity is heavily influenced by the surface chemistry and chemical speciation of thallium in fly ash. In this work, XANES was used in combination with leaching tests to determine the fundamental nature of thallium attachment to fly ash to discern speciation, the environmental implications of thallium leaching, and to quantify thallium leaching under various environmental conditions.

This work aims to give information on the intrinsic leaching behavior of different ashes through leaching tests and XANES. Information regarding thallium leaching in aquatic environments has the potential to be used to project long-term cumulative release of this element from fly ashes under various management scenarios. Furthermore, this research can be used to develop better recovery and minimization technologies once an optimal set of conditions is known.

Experimental Methodology

Overview of method options

Several leaching test methods were considered for this research including the US EPA Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP), but the Kosson Framework seemed to be the most appropriate and thorough. The TCLP predicts leaching behavior based on a fixed single pH and L:S ratio to reflect the chemical environment of a municipal solid waste landfill. This fly ash is not disposed of in municipal waste landfills, so that test would not have given relevant results. The SPLP mimics leaching under rainwater runoff conditions under one pH and L:S ratio. This test is appropriate insomuch as the only simulated influent flow is rainwater, but it cannot examine variable pH and L:S ratio. On the other hand, the Kosson Integrated Framework is a three-tiered system of tests

and can be varied depending on the management scenario (Kosson). The three tiers are as follows: Tier 1-Screening based assessment, Tier 2- Equilibrium based assessment, and Tier 3-Mass Transfer based assessment. The Kosson Integrated Framework provides intrinsic leaching parameters that are highly realistic and minimally conservative. Specifically, Tier 2 will generate data regarding leaching behavior under variable L:S ratios and pH and is the primary testing methodology used in this thesis.

To examine the different surface chemistries of fly ashes, several fly ashes from Ohio and West Virginia in addition to the main fly ash from the primary methodology were examined with XANES at the Argonne National Laboratory. I chose these particular ashes to test because the different leaching behaviors may correlate to different thallium surface chemistries.

pH Evaluation Method

The Tier 2 test SR002.1 (Alkalinity, Solubility and Release as a Function of pH) was chosen at first because it is thorough in evaluating pH effects at a constant L:S ratio of deionized water to fly ash through "11 parallel extractions of particle size reduced material at a liquid-to-solid ratio of 10 mL extractant/g dry sample. An acid or base addition schedule is formulated for eleven extracts with final solution pH values between 3 and 12, through addition of aliquots of HNO_3 or KOH as needed." (Kosson) However, after discovery of the immense acid neutralizing capacity of the fly ash, it became clear that it was impossible to maintain a constant pH during a 48 hour leaching period. Another test, EPA method 1313, is based on the same concept as SR002.1: variable pH, but relies on the end pH of the leachate rather than maintaining a given pH throughout a 48 hour period as in SR002.1. In order to be conservative, practical, and consistent, I chose to leach the samples over 48 hours. I performed this test in two phases: pre

method and final. For Pre Method 1313, I added various amounts of acid and base to make a solution of constant volume to suspend the fly ash in as detailed below in Table 2.

Table 2: Pre method addition schedule & resulting pH values

Sample #	1	2	3	4	5	6	7
Fly ash (g)	20	20	20	20	20	20	20
+mL 2N HNO_3	0	0	0	0	10	15	20
+mL 1N NaOH	40	30	20	0	0	0	0
+mL DI	160	170	180	200	190	185	180
Total Volume (mL)	200	200	200	200	200	200	200
pH	13.10	13.00	12.65	8.11	1.61	1.24	1.03

After the additions were made, the vessels were placed in a custom made rotator to rotate at 28 rpm for 48±2 hours. After the rotation, pH was measured to discover which acid/base addition resulted in attainment of a target pH within 0.5pH units. The pH meter has been calibrated just before each use using buffered solutions of 4.00, 7.00 and 10.01. After the pre method, I chose the additions correlating to a range of pH values and ran the experiment in triplicate, but with a total volume of 50 mL. If any of the pre method trials resulted in an acceptable pH, they could be treated as a sample, filtered and analyzed for total thallium.

Figure 2: Pre Method 1313 samples in rotator

Table 3 details additions to the vials

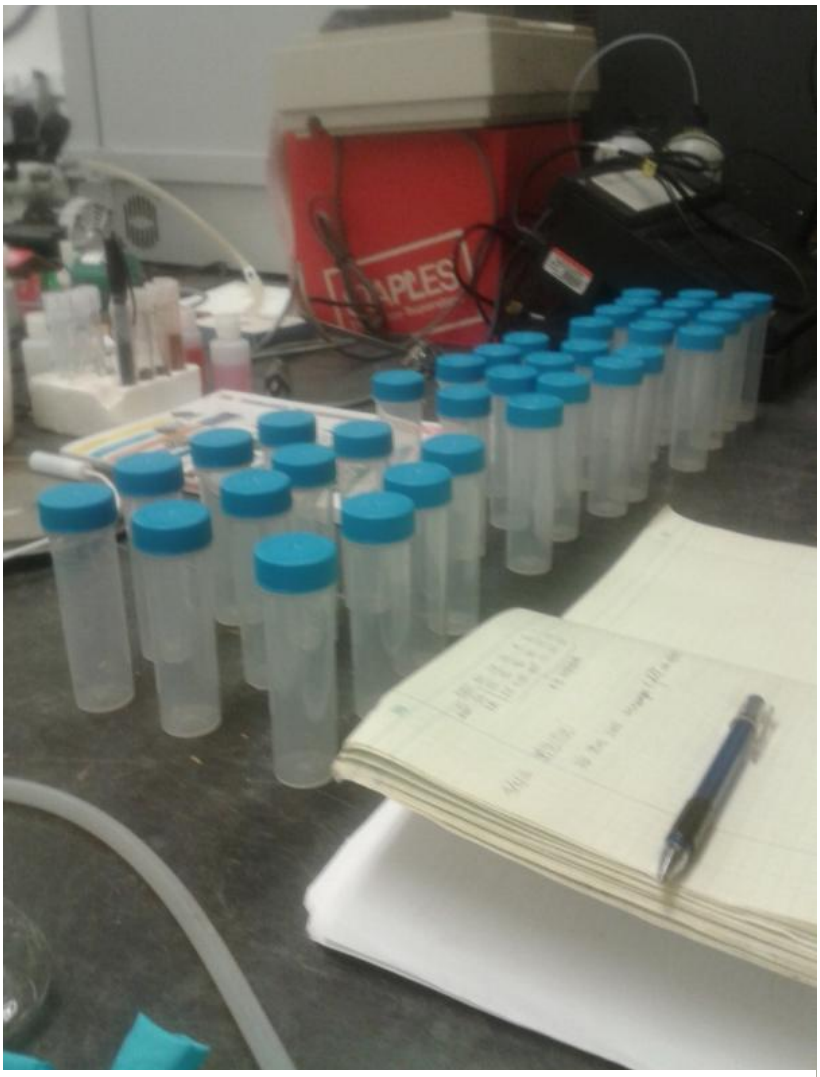

Figure 3: Vessels used for method 1313

seen in Figure 3 used in the final method 1313 test. Each sample was filtered through an EPA-approved TCLP Method Millipore AP40, pore size 0.7 micron, depth filter. Each filter was washed with one 100 mL aliquot of 5% HNO_3 followed by three 100 mL aliquots of deionized water before the sample was filtered. These filters are unique in that they are made of glass fiber and contain no resin binders that could contaminate analysis (EMD Millipore Corporation). The washing procedure was repeated with each new filter for each sample. The eluate was collected and preserved with approximately 5% concentrated HNO_3 to prevent thallium precipitation at high pH values. A cloudy white vapor or gas was evolved during preservation of the samples treated with the sodium hydroxide. The preserved triplicate eluate samples were then analyzed for total thallium via graphite furnace atomic absorption spectroscopy, as described later.

Table 3: Method 1313 addition schedule

Sample #	1	2	3	4	5	6
Fly ash (g)	5	5	5	5	5	5
+mL 2N HNO_3	0	0	0	2.5	3.75	5
+mL 1N NaOH	10	7.5	5	0	0	0
+mL DI	40	42.5	45	47.5	46.25	45
Total Volume (mL)	50	50	50	50	50	50

Variable Liquid to Solid Ratio Evaluation Method

In Tier 2 of the Kosson Integrated Framework, SR003.1 (Solubility and Release as a Function of L:S Ratio) examines the effect of variable L:S ratios through "five parallel batch extractions over a range of L:S ratios (i.e., 10, 5, 2, 1, and 0.5 mL/g dry material), using deionized (DI) water as the extractant with aliquots of material that has been particle size reduced." (Kosson). Since fly ash is already homogeneous in size and sufficiently small (2-20 μm or .008-.08 thousandths of an inch), there was no need for size reduction (EPRI). Also, earlier trials with the specified L:S ratios did not produce leachate from the 0.5 mL/g dry material sample, while analyses via graphite furnace atomic absorbance spectroscopy of the remainder suggested that a ratio between 10 and 20 would lower the leaching of thallium to acceptable levels. Therefore, the final trial (performed in triplicate) included L:S ratios of 20, 16, 10, 5, 2, and 1. The additions necessary to attain specified ratios measured in the final experiment are shown in Table 4.

Table 4: SR003.1 additions

Ratio	20	16	10	5	2	1
Fly ash (g)	2.5	3.125	5	10	12.5	25
+ mL DI	50	50	50	50	25	25
Total Volume (mL)	50	50	50	50	25	25

Graphite Furnace Atomic Absorption Spectroscopy Total Thallium Measurement Method

The graphite furnace apparatus described in Figure 4 was used with a thallium hollow cathode tube shown in Figure 5 within the Agilent Varian SPECTRAA880 Atomic Absorption Spectrometer pictured in Figure 6. This instrument was chosen because of its extremely low detection limits. GFAAS can attain ppb measurements with high accuracy due to the lack of large dilutions involved in introducing the sample to a flame (as in traditional flame atomic absorption methods). Instead of using a flame to atomize a 10 mL sample, GFAAS uses a carbon tube approximately 1 cm in length and 5mm in diameter to rapidly heat a μL sample. Less dilution correlates to higher sensitivity.

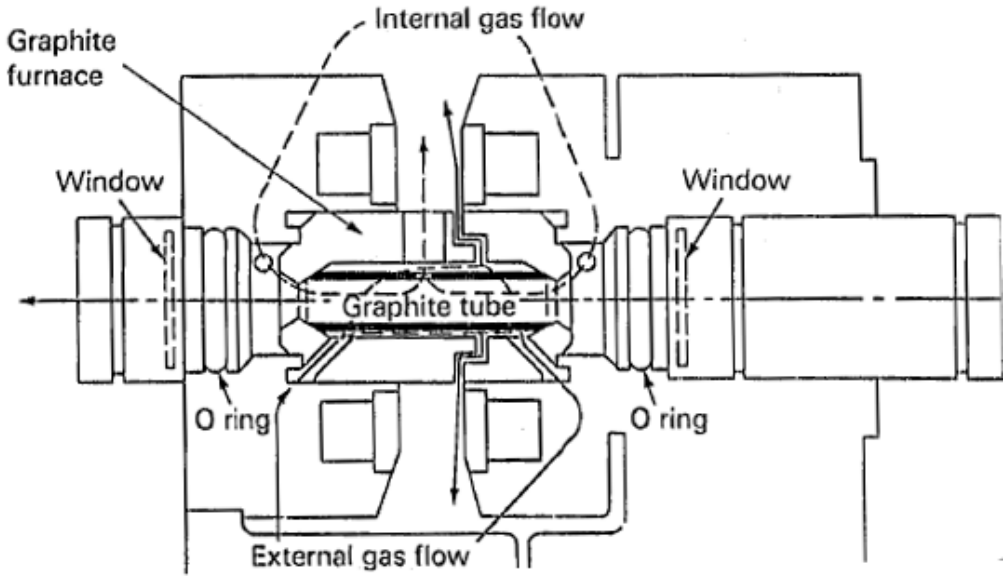

Figure 4: Schematic of graphite furnace apparatus (Slavin)

The GFAAS and other atomic absorption instruments get their specificity from a hollow thallium cathode lamp. The thallium hollow cathode lamp is composed of a hollow thallium

cathode enclosed in glass next to a tungsten anode under a nonreactive argon environment to generate thallium excitation energies. These thallium excitation energies will only excite the thallium electrons on thallium atoms in the sample.

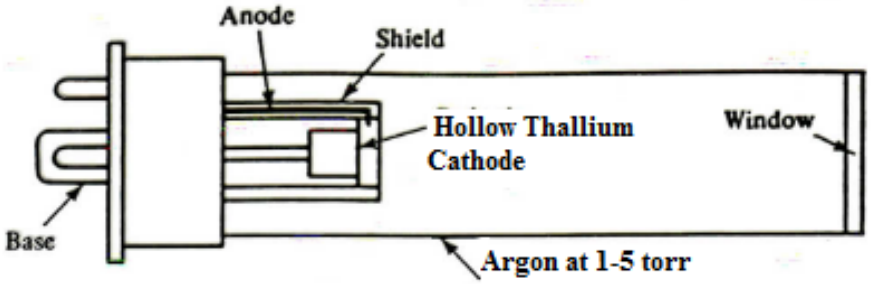

Figure 5: Cross section of a thallium hollow-cathode lamp (Slavin)

Additionally, GFAAS was the recommended method used for detection of environmental levels within fly ash (EPRI). The SPECTRAA software processing program was used for data processing.

Figure 6: GFAAS

All samples were preserved with 5% concentrated nitric acid to assure all thallium leached remained in the soluble form and did not precipitate throughout the analysis period. Furthermore, a combination of check standards, method blanks, filter blanks, and analysis blanks were incorporated into the analysis between triplicate sample testing to assure minimum drift and accurate measurements. The method used involved taking each sample, analyzing it twice and reporting the mean value as the measured value. 5% nitric acid was used as a make-up, a 75ppb thallium solution preserved with 5% nitric acid was used as the standard, and 250 ppb palladium with citric acid as the reducing agent was used as the matrix modifier. A calibration curve was first constructed from the standard and is included in Appendix C: Calibration Curve and associated data. The method was also set up to automatically dilute the sample if initial analyses showed it to be out of the range of the calibration curve.

Synchrotron Test Method

Figure 7:DND CAT beamline

The Advanced Photon Source (APS) at Argonne National Laboratory was utilized for XANES analysis. The beam line 5BMD was used at the DND-CAT beamline seen in Figure 7. The beamline engineer is Dr. Qing Ma. The majority of the first day was spent optimizing scanning conditions. Once these were optimized, adsorption data for one sample was obtained after 98 minutes collection time. The following is the summary of the testing.

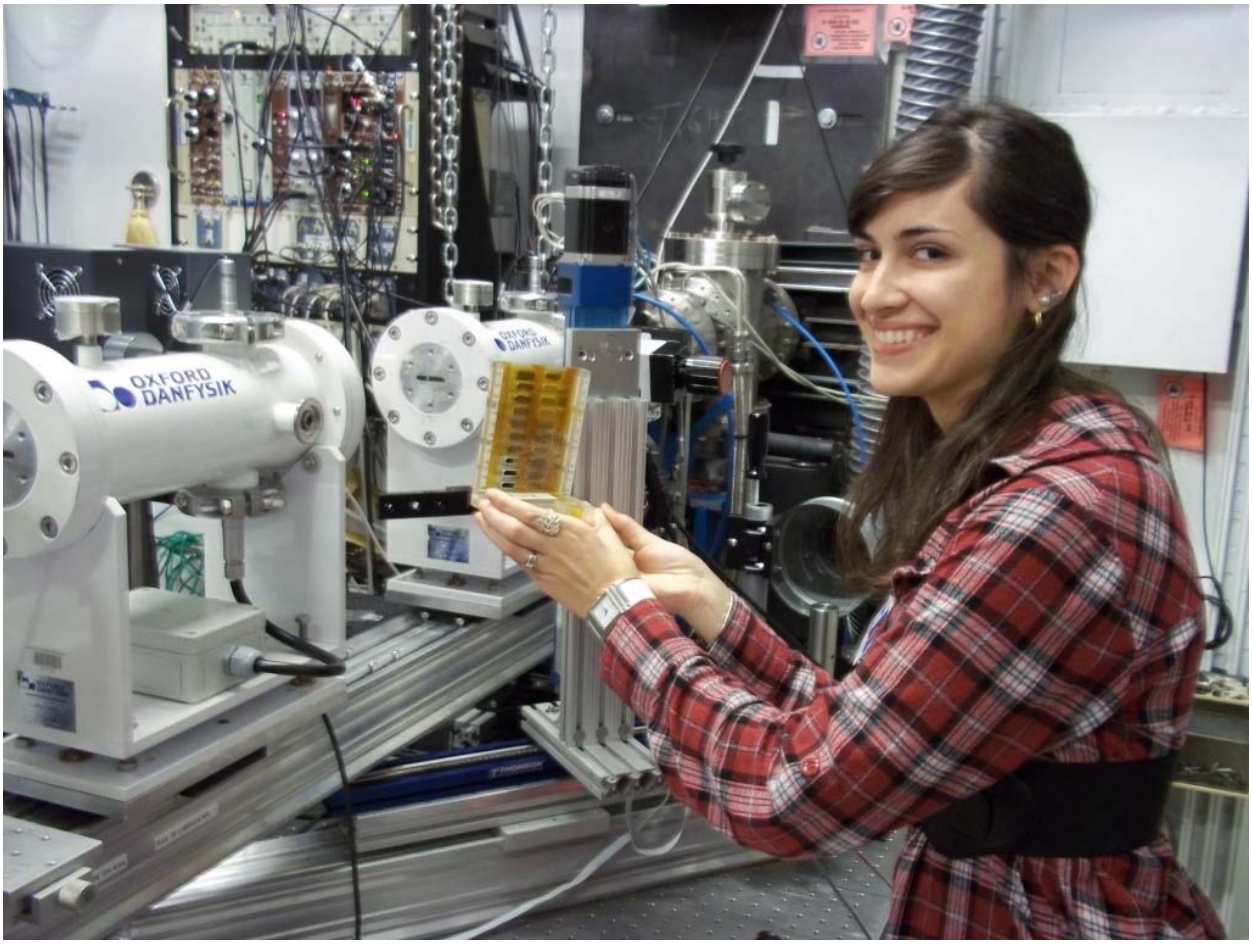

Figure 8: Sample placement across from fluorescence detectors in ionization chamber

All untreated samples were scanned in the evening of day one. Fly ash samples including the primary fly ash from the previous tests were treated with different leaching procedures and then

were placed in a custom built plastic holder and sealed with special tape. Figure 8 details the sample placement in the hutch.

The beam enters through the metallic pipe structure (optical chamber) that focuses and collimates it located near to the wall, passes through the horizontal slit and only irradiates one sample at a time. Concentrated samples can give a strong enough signal to allow measurement of absorption alone. In that case, transmittance through the sample is measured by a detector behind the second ionization chamber and concentration is based on intensity drop. However, the fly ash samples with levels of thallium between ppm and ppb were considered to be of very low concentration. For this type of sample, fluorescence gives better results. The fluorescence detectors were placed at 45 degree angles to the sample in order to maximize photon count.

During day two, four leached samples (20:1 SPLP leached Primary, 10:1 SPLP leached Primary, 2:1 SPLP leached Primary, and 20:1 DI leached Primary) were selected to have their first scan. After that, four samples (Primary, and fly ashes 1, 2, and 3) were selected for two additional scans based on the jump magnitude on the adsorption edge. These duplicate scans were carried out overnight.

Day three was when scanning of references occurred. Three references were chosen for scanning in order to garner qualitative information regarding which peaks correlated to which complexes. The three references were made by adding 0.6 wt% of $TlCl_3$, TlCl, and Tl_2O_3 standards individually to three untreated samples of the primary fly ash. After those scans, two more scans were performed on the four selected untreated samples. Overnight, two more scans on the four leached samples and one more scan on the Primary fly ash were performed.

To summarize, 4 scans were performed on the untreated Primary fly ash. Three scans on Fly ash 1, 2, and 3 untreated samples were performed. Additionally, three scans were performed on

the 20:1 SPLP leached Primary, 10:1 SPLP leached Primary, 2:1 SPLP leached Primary, and 20:1 DI leached Primary fly ash samples. Only one scan was done on the remainder of the untreated samples. The data was processed using the ATHENA software downloaded from the Argonne National Laboratory website.

Results & Discussion

Data Treatment

The raw data along with the treatment from the pH and variable L:S ratios can be found in Appendix B: Total Thallium Analysis Data. I chose not to group data from the previous L:S test from 5.3.2011 with the final data because it was considerably lower than the triplicates. This is most likely because the samples were acidified with 2% concentrated HNO_3 while the final data was acidified with 5% concentrated HNO_3. Acidification guarantees all thallium will be in solution. Data from the pH test on 4.9.2012 was incorporated into the graph because it was consistent with the data gathered on 4.11.2012.

pH Test Results

Figure 9 illustrates the relationship between total thallium release at the end of the leaching period as thallium in micrograms per liter, parts per billion, and varying meq additions. Figure 10 demonstrates this relationship in terms of end pH resulting from the meq additions. Figure 11 demonstrates the impact of changing pH on thallium release per gram of dry fly ash. The arithmetic mean of at least three analyses is plotted in all of the graphs. The source data are located in Appendix C: Total Thallium Analysis Data in data table C-3. The error bars represent the standard deviation among similarly treated samples. Note that some error bars are so small that they are within the marker borders.

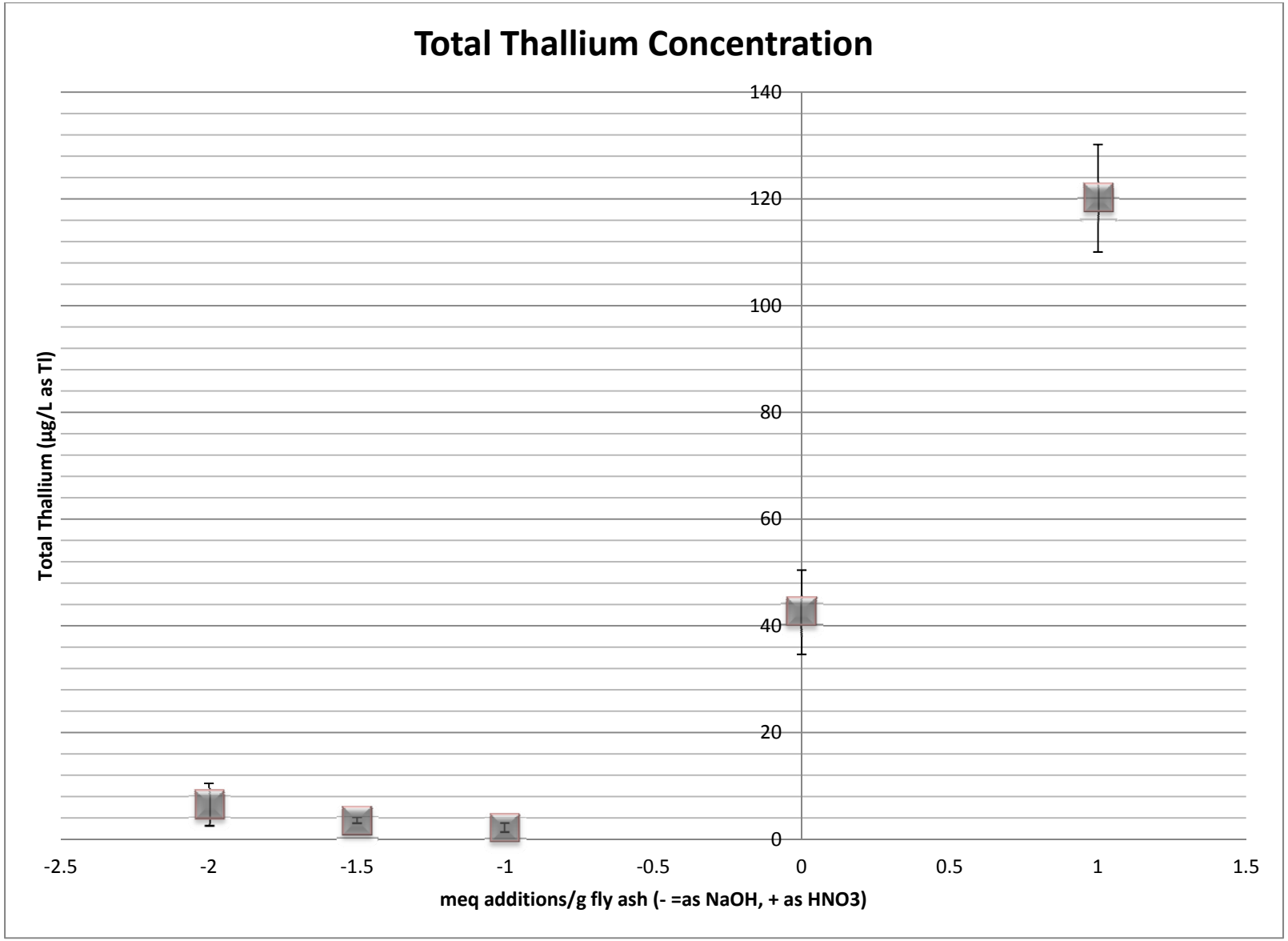

Figure 9: meq additions of acid and base have an impact on total thallium concentration leached

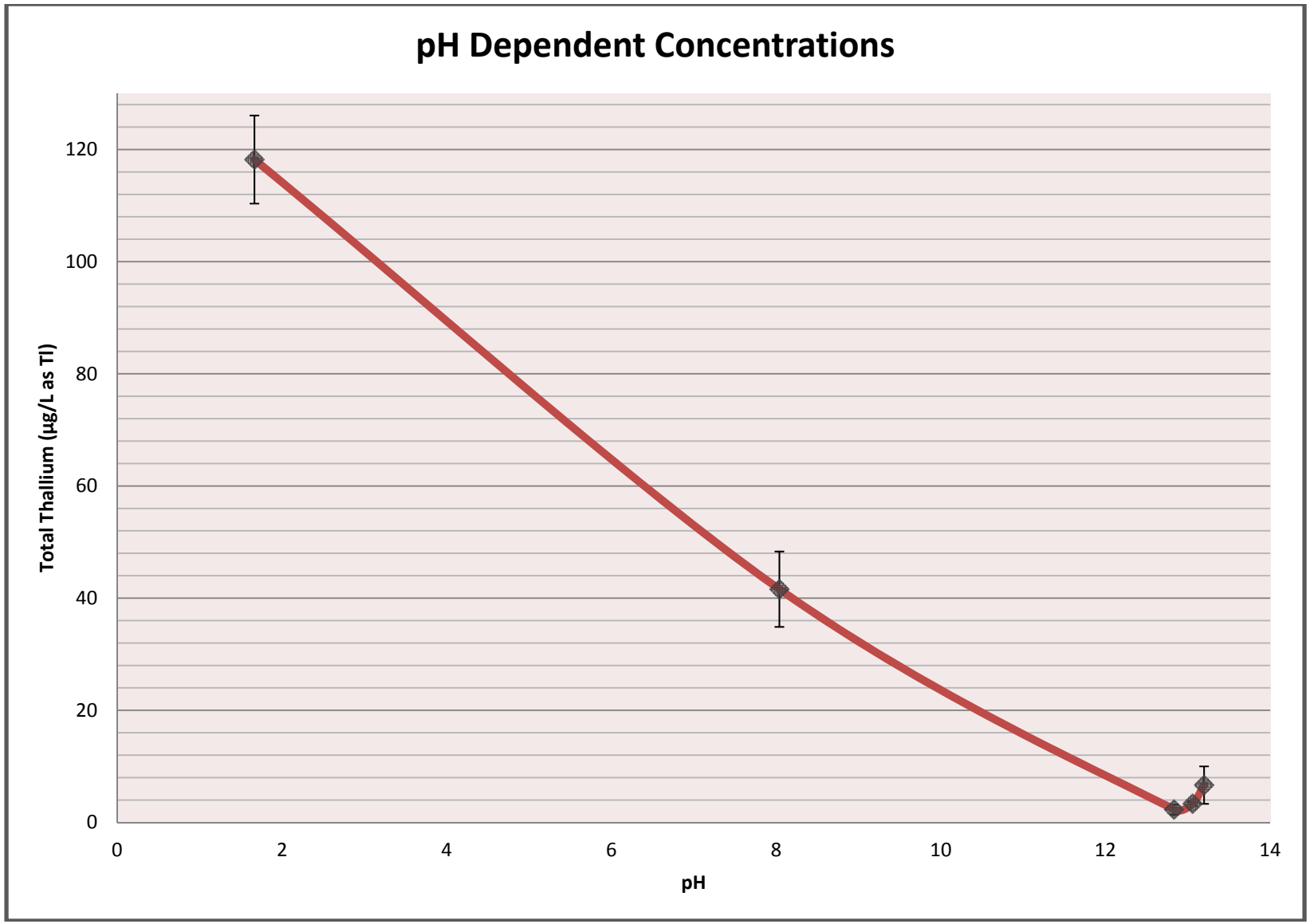

Figure 10: pH influence on total thallium concentration released during leaching

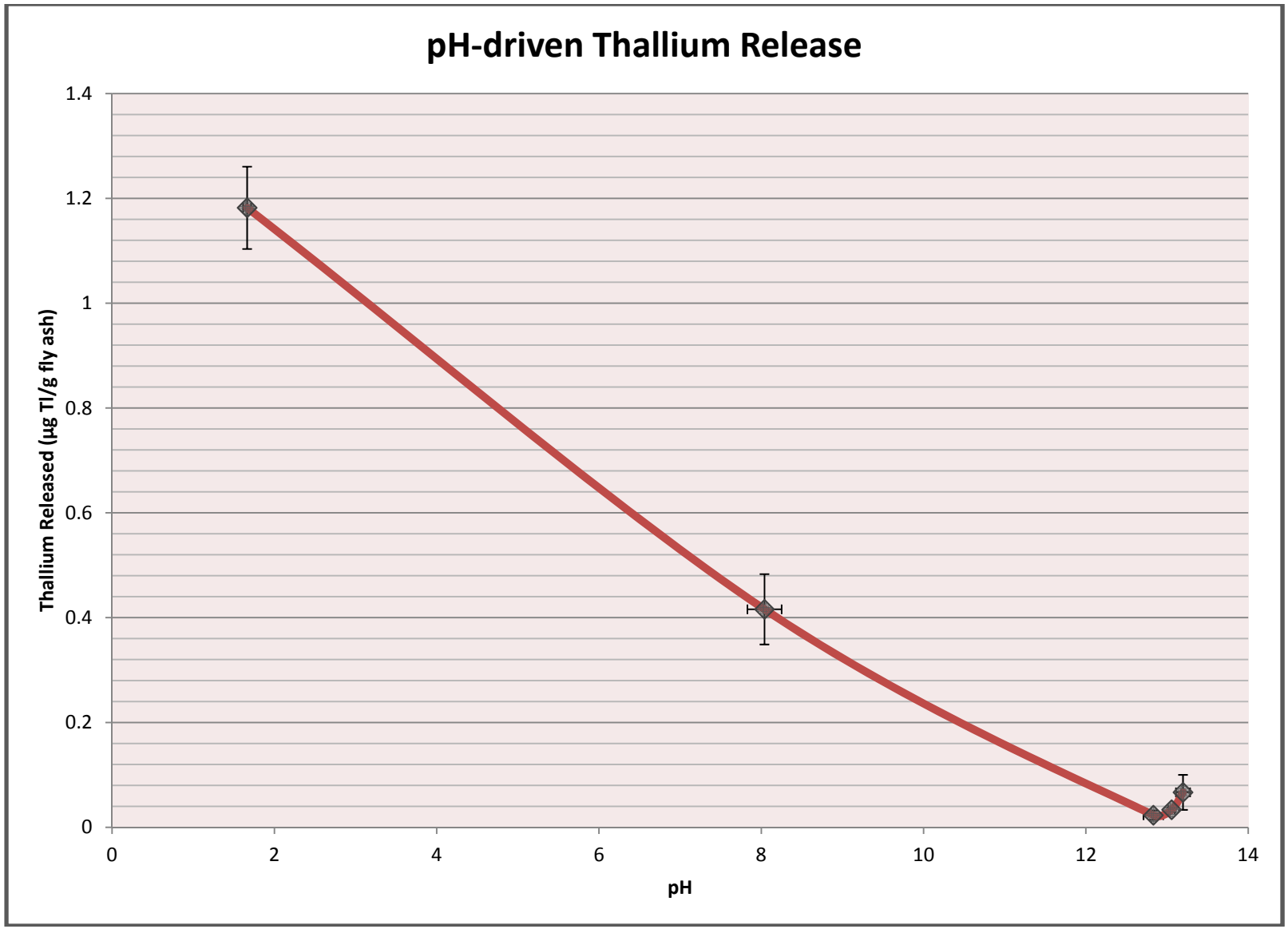

Figure 11: Normalized pH driven thallium release during leaching as a function of pH

L:S Test Results

Initial results depicted in Figure 11 suggest an acceptable drinking water level will be achieved by a L:S value of around 15 so greater ratios were tested in the final iteration. Figure 12 shows the influence of varying L:S ratios on total thallium release as thallium in micrograms per liter, parts per billion. Figure 13 illustrates this relationship in terms of thallium release per gram of dry fly ash. As in the pH graphs, the arithmetic mean of triplicate samples is plotted in each graph. The error bars represent the standard deviation among the triplicate samples. Note that some error bars are so small that they are within the marker borders.

Also, note the slight similarity in the graph's shape to initial results.

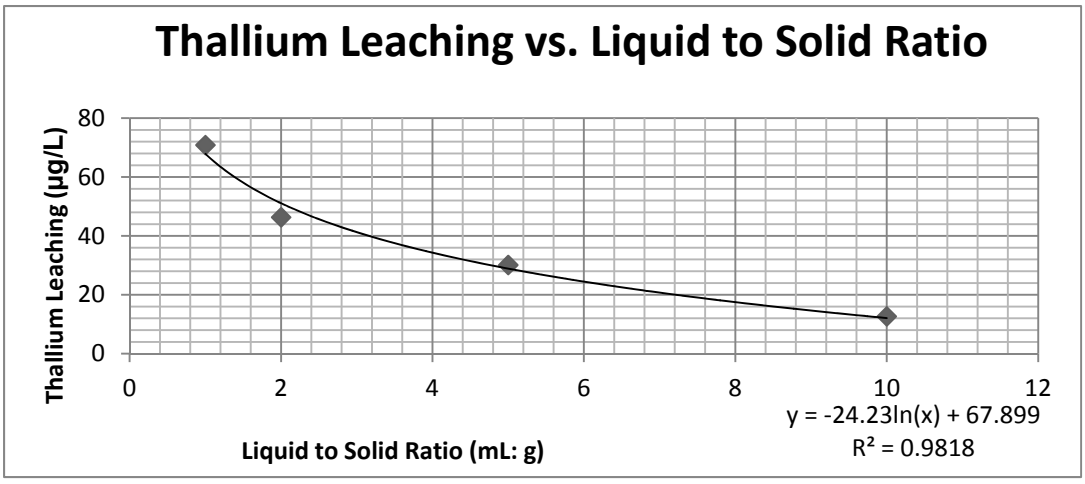

Figure 12: Preliminary L:S results, filtered through .45 micron filter and acidified with 2%HNO3

Table 5: Values and quality control checks of preliminary L:S results

Sample	Total Tl (ppb)
QC 25ppb	24.582
Blank	0.452
Ca10LS	12.669
Ca5LS	30.133
Ca2LS	46.334
Ca1LS	70.859
Control LS	1.332
Filter Blank	1.022
QC 25ppb	26.774

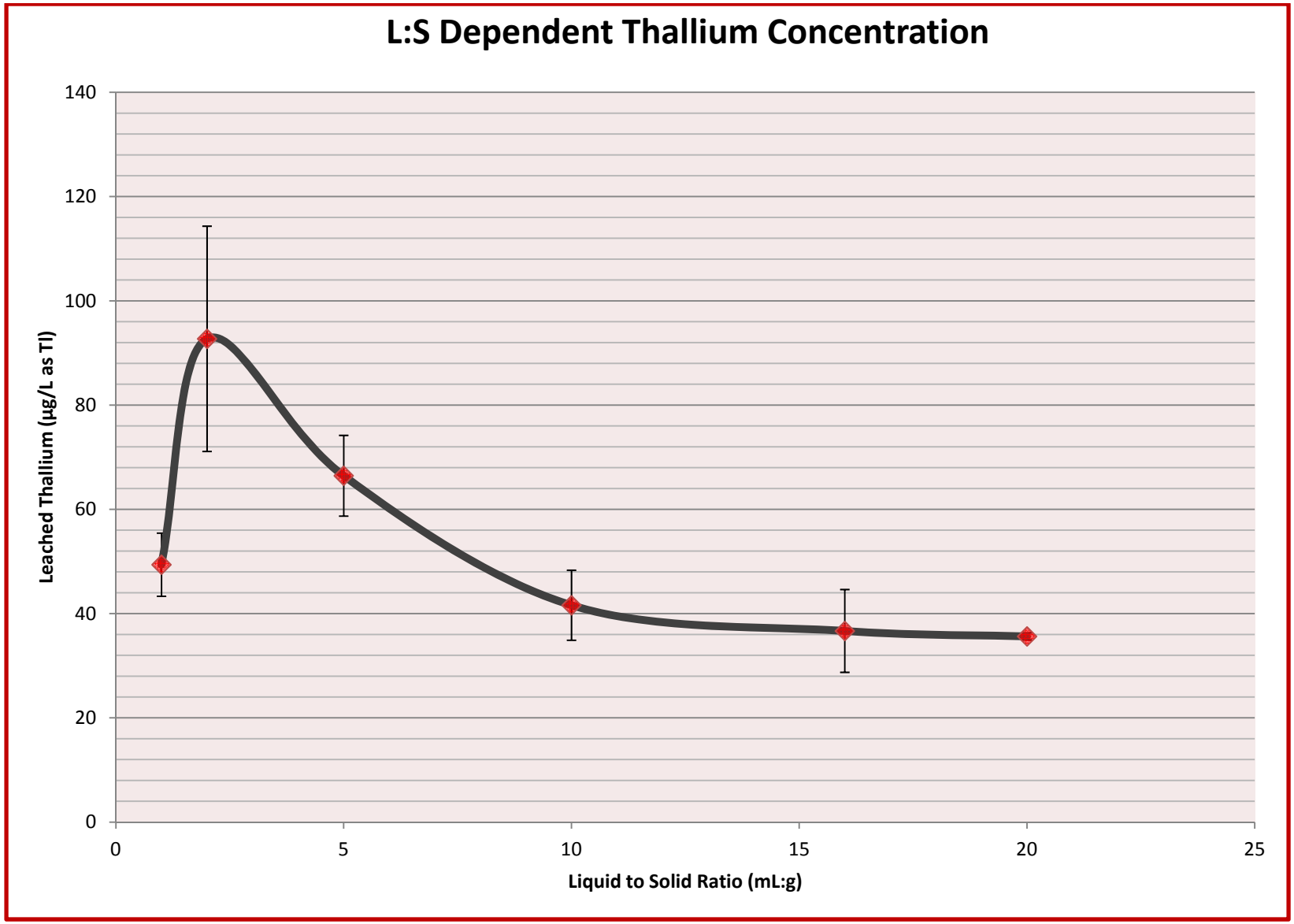

Figure 13: L:S ratio effect on total thallium concentration leached into solution

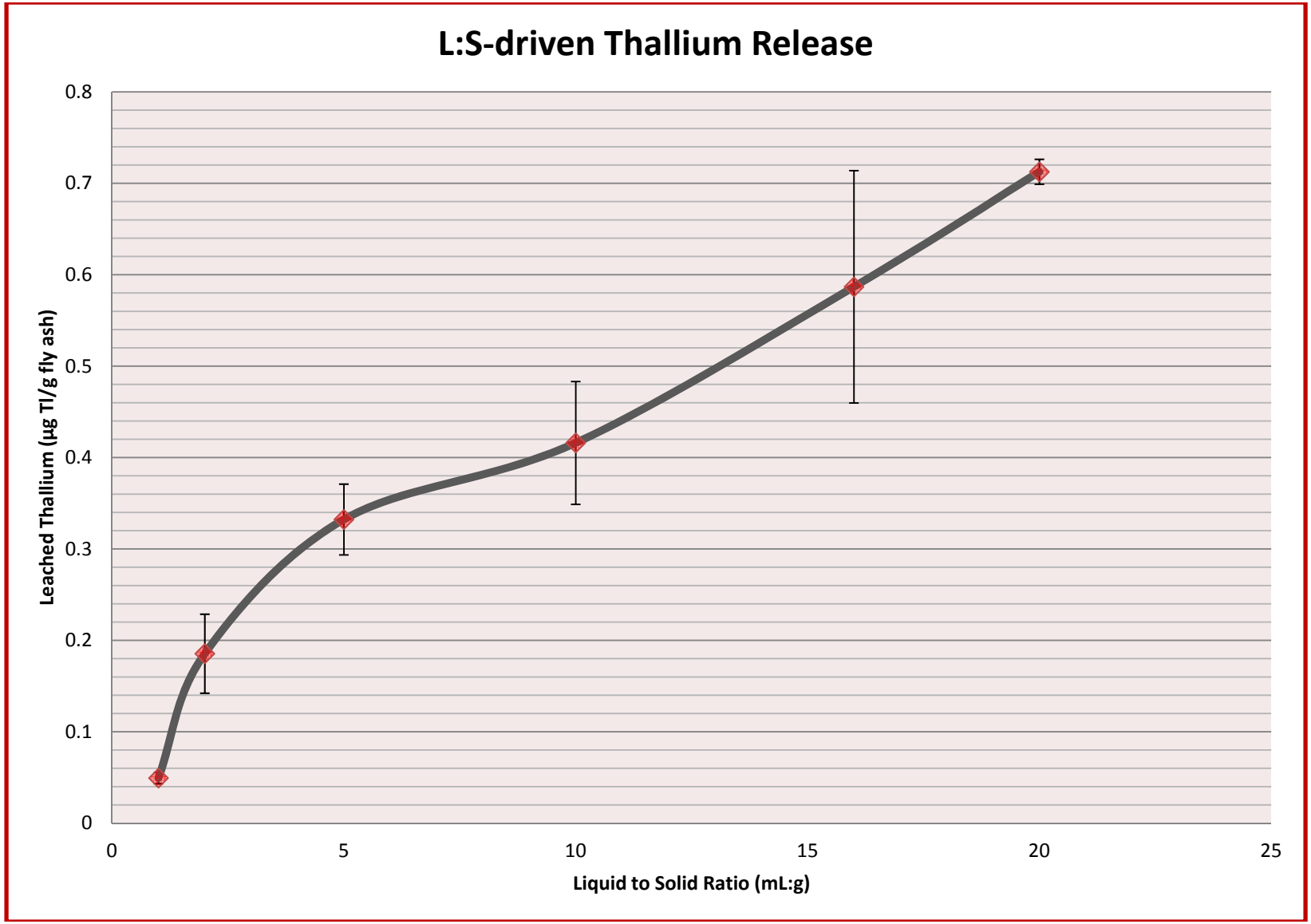

Figure 14: Variable L:S ratio driven thallium release by each gram of fly ash over the leaching period

Synchrotron Results

Figures 15, 17 and 19 are normalized scans of the samples. They give information about the relative quantities of thallium speciation. Their derivatives are shown in Figures 16, 18 and 20 so that the peaks are more distinct. Note the similarity between the thallium (+3) species curves illustrated by the thallium oxide and chloride compounds. Chloride compounds were measured because it is a common salt and is present in the fly ash. TlCl would be very easily dissolved and would describe some of the leaching if the compound were thallium(+1). Thallium oxides were tested because oxides form from high temperatures experienced during combustion.

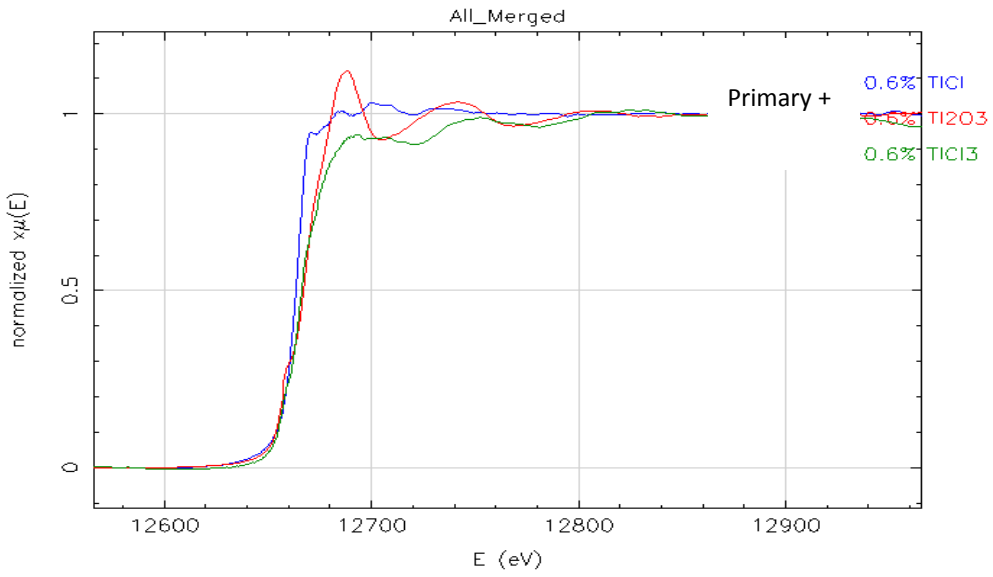

Figure 15: Scan of Primary fly ash without any treatment with various additions

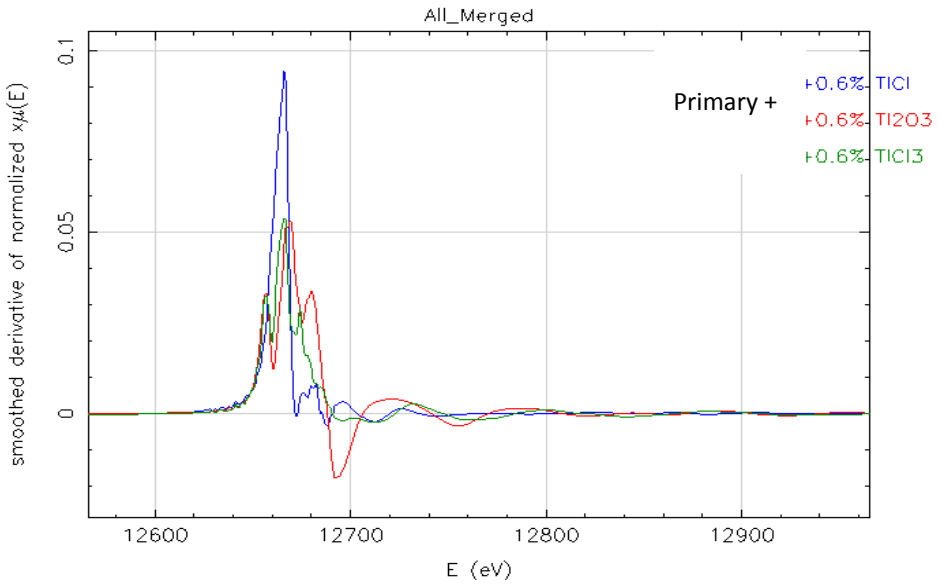

Figure 16: First derivative of Cardinal fly ash scan without any treatment with various additions

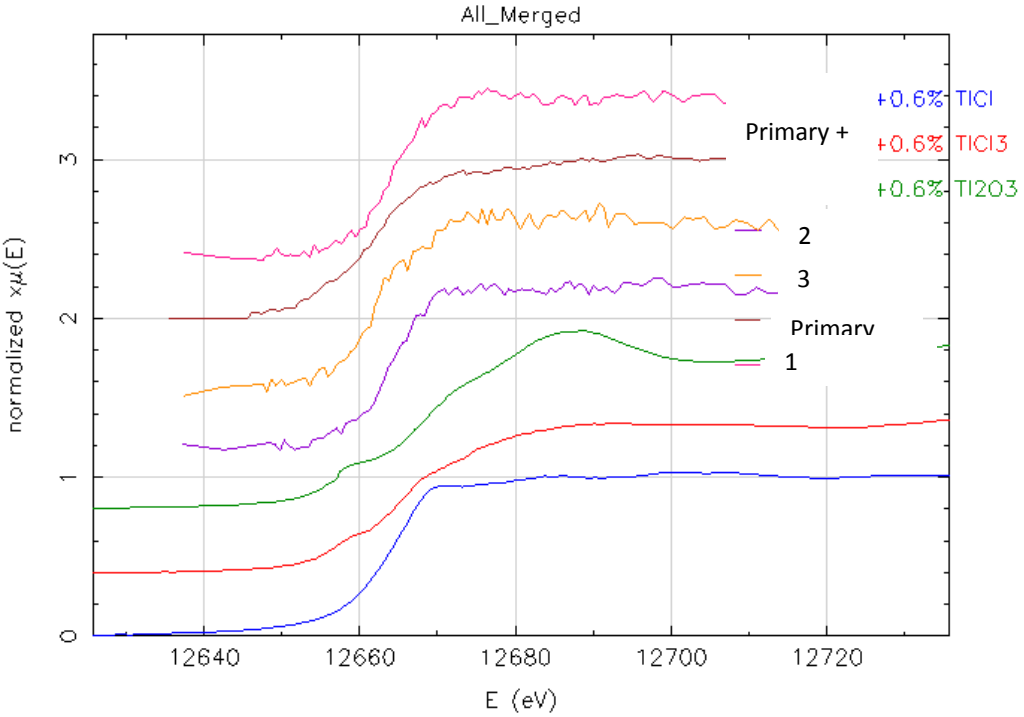

Figure 17: Scan of Various Ashes compared with various standard additions

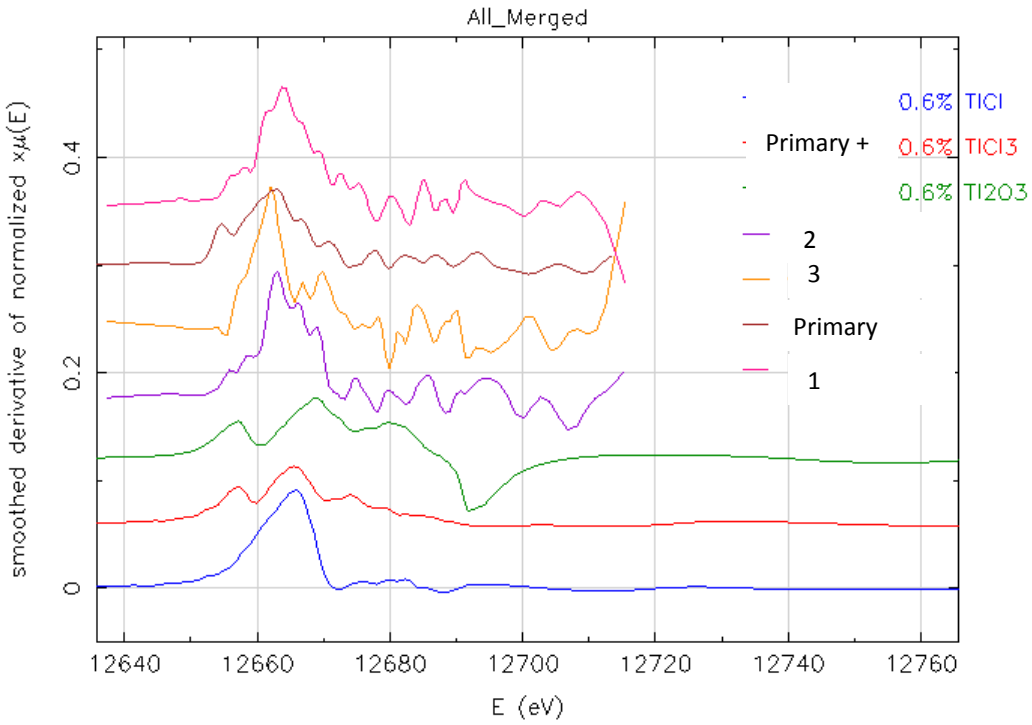

Figure 18: First derivative of Various Ashes compared with various standard additions

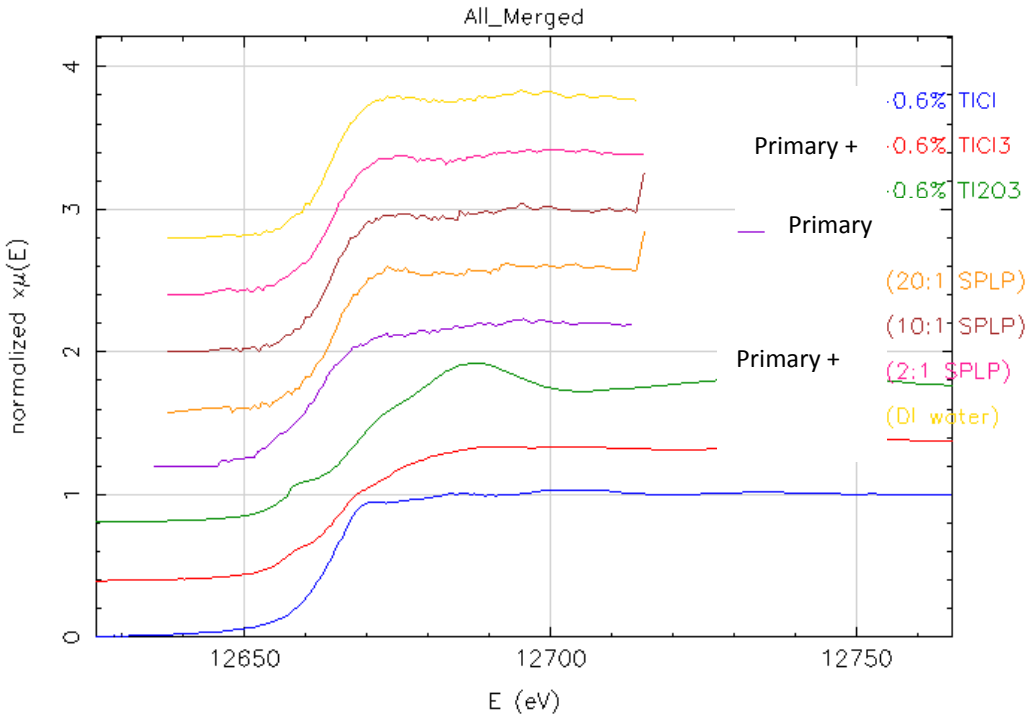

Figure 19: Scan of several different treatments of Cardinal fly ash compared with various standard additions

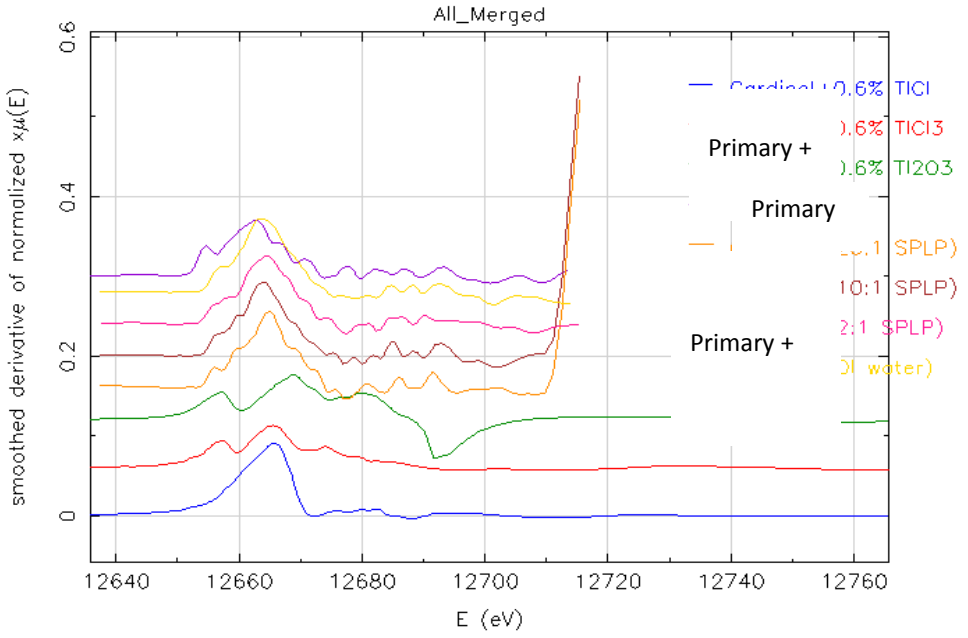

Figure 20: First derivative of several different treatments of Cardinal fly ash compared with various standard additions

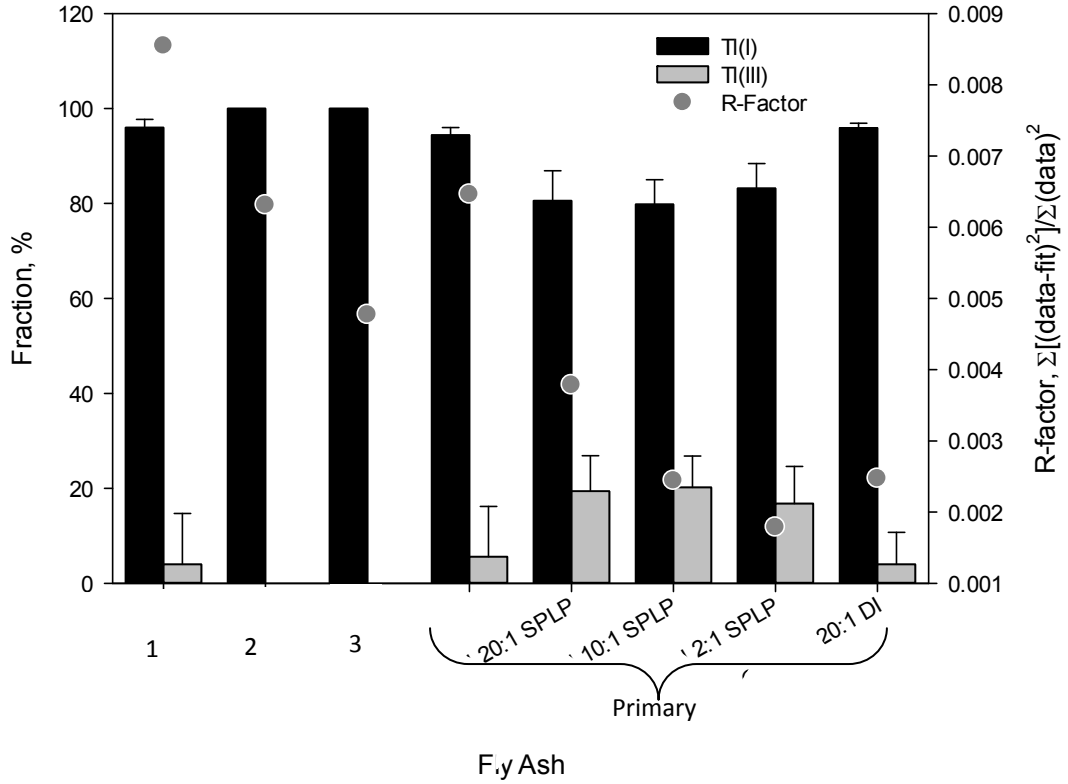

Figure 21: Approximate speciation of various fly ashes and various treatments to Primary fly ash

Note that >95% of the thallium in the untreated fly ash takes the monovalent form while the acid leached samples contain thallium that is approximately 20% trivalent and 80% monovalent, regardless of solid to liquid ratio.

Analysis

pH Result Analysis

Closer examination of Figure 9 shows that the minimum total thallium leaching is correlated to addition of only a 1 meq of base per gram fly ash. Figure 11 has a similar shape except with a minimum at pH of approximately 13 with very high leaching at low pH values and increasing thallium leaching at pH>13. Possible explanations for this trend include presence of a thallium hydroxide complex, mineral phase dissolution, and equilibrium chemistry.

Metallic hydroxides also exhibit this trend. It is a likely possibility since thallium has a high tendency to complex with other metallic anions and minimum thallium release is provoked by high concentrations of hydroxide.

An alternate explanation is the dissolution of mineral phase throughout the release. Acidic pHs often result in mineral dissolution. If the thallium is fixed within a mineral, it would make sense to decrease as dissolution of that mineral decreases with increased pH. However, the pH dependence of this dissolution is highly dependent on the mineral type. Some minerals are soluble at high pH.

Alternately, there could exist a thallium(+1) or (+3) complex in equilibrium with a soluble anion during low pH conditions and an insoluble anion around pH 13.

This behavior is also characteristic of desorption processes. If thallium is mainly adsorbed to the surface of the particles, elevated pH would inhibit release while large releases would be observed at low pH.

Alternately, these mechanisms could be combining to result in the observed trend. Regardless, the results suggest that thallium leaching could be minimized by the addition of one meq of base per gram of fly ash disposed of in the pond if there is approximately 10 times more water than there is fly ash.

L:S Result Analysis

As seen in Figure 2, the effect of Liquid to solid ratio on thallium leaching plateaus at a value of about 28 ppb for ratios greater than 10. A combination of dissolution, adsorption, and equilibrium mechanisms is most likely responsible for the observed trend.

If dissolution alone was the main mechanism, there would be no relationship between concentration and L:S ratio. This is because of the solubility constant. If the equation governing this behavior was,

$$TlCl \leftrightarrow Tl^{+} + Cl^{-}$$

the solubility would depend only on the amount of Tl and Cl, and remain independent of the amount of solid to dissolve as long as the solid is present in excess since:

$$K_{sp} = [Tl^{+}][Cl^{-}]$$

However, Figure 12 is definitely not a straight line so dissolution is most certainly not the main mechanism at play here. A cursory glance at Figure 13 would give the impression of dilution during the range between L:S ratios of 2-10. Figure 14 contradicts that mechanism because leaching per gram of fly ash increased through the increase in L:S ratio.

Adsorption is not the main driver of this release either because adsorption kinetics fail to explain the trend shown in Figure 14. Adsorption kinetics say that high concentrations of thallium in solution result in particle surface loading so that at a certain threshold L:S ratio, the surface sites have been filled and the remaining thallium in solution begins to dilute. Figure 14 would exhibit downward concavity throughout if the main driver were adsorption.

Perhaps diffusion/limited accessibility could be the mechanism to explain the trend in Figure 14. The increase in total thallium between L:S 1 and 2 could be due to dissolution of the most easily accessible thallium complex on the surface of the particles. The slower increase between L:S 2 and 5 could be due to competition between dilution and diffusion-that is-water penetrating the fly ash particles causing thallium to be released in a quantity directly proportional to the amount of water available. Other metals have been observed exhibiting this trend, though, and it is the very reason why conservative regulatory tests are performed at L:S ratios of 20 (DeGraff) (US EPA).

These results suggest that varying liquid to solid ratio alone will not attain levels acceptable for drinking.

XANES Analysis

The size of the jumps in Figures 15, 17 and 19 give information about the relative quantities of total thallium in the samples tested. The spikes in figures 16, 18 and 20 in the standard lines are characteristic of the standards. Appearance of these spikes in other lines indicates probability of the compound in that sample at a comparable level. The lack of spikes similar to these indicates that the respective thallium compounds either a) are not present at comparable levels or b) are obscured by noise. Considering these possibilities together with evidence produced by the

pH and L:S tests suggests that the standards are probably not present in the samples at comparable levels. However, Figure 21 is a clear indication of the speciation fractions of thallium in leached samples and unleached samples. This suggests that the acid interaction plays a role in thallium (+3) generation.

Conclusions & Future Directions

I expected to gain information on the intrinsic leaching behavior of different ashes and the thallium leaching to be a function of pH and liquid to solid ratio through carrying out this work. I did discover minimum concentrations on ppb by volume and ppb by weight released in response to changing pH and L:S ratios. On a ppb (volume) basis the minimum leaching was between L:S ratios of 10-20, and 1 on a mass ppb basis. Minimum release occurred at pH 13, or a dose of 1 meq base/g fly ash in 10 mL water. The advanced photon source suggested identification of the majority thallium complex before leaching as thallium(+1). Furthermore, the results suggested that SPLP leaching has a transformative effect on a small fraction of thallium from thallium(+1) to thallium(+3) relatively constant regardless of L:S ratio.

Future work could involve returning to Argonne National Laboratory to perform more scans in order to improve the signal to noise ratio. Additionally, assuming the measured scans from this work are accurate, a future hypothesis could be that thallium release is due to diffusion/limited availability equilibrium. Furthermore, to determine whether existing thallium (+1) is converted to thallium (+3), scans could be performed on fly ash sample 1, entirely composed of Tl(+1). Also, surface chemistry could be better elucidated by more scans of more standard additions to the fly ash by the APS; perhaps thallium hydroxide or a thallium copper compound. Furthermore, more data points could be gathered to minimize the standard deviations so that all of them are too small to discern without transparent data markers.

Bibliography

DeGraff, J.V. *Understanding and Responding to Hazardous Substances at Mine Sites in the Western United States*. Geological Society of America, 2007.

Dewan, Shaila. "Tennessee Ash Flood Larger Than Initial Estimate." *The New York Times* 26 December 2008. Electronic Archive. <http://www.nytimes.com/2008/12/27/us/27sludge.html>.

Dr. Robert Peltier, PE. *Trona Injection Reduces SO3 Emissions*. 31 July 2008. 6 April 2011. <http://www.coalpowermag.com/environmental/138.html>.

EMD Millipore Corporation. *Millipore Technical Library*. 2012. 23 4 2012. <http://www.millipore.com/faqs/tech1/4y7lg6>.

EPRI. *A Limnological Approach to the Management of Fly Ash Disposal Ponds*. Palo Alto, CA: Electric Power Research Institute, 2004.

—. *Chemical Constituents in Coal Combustion Product Leachate: Thallium*. Palo Alto, CA: EPRI, 2008.

—. *Coal Ash: Characteristics, Management and Environmental Issues*. Palo Alto, CA: EPRI, 2009.

—. *Groundwater Quality at Power Plants in West Virginia*. Palo Alto, CA: EPRI, 1999.

—. *Integrated Fly Ash Pond Management*. Palo Alto, CA: EPRI, 2009.

International Programme on Chemical Safety. "Environmental Health Criteria 182: Thallium." 1996.

Kirk G Scheckel, Enzo Lombi, Steven A Rock, Mike J McLaughlin. "In Vivo Synchrotron Study of Thallium Speciation and Compartmentation in Iberis intermedia." *Environmental Science and Technology* 38 (2004): 5095-5100.

Kosson, Van Der Sloot, Sanchez, Garrabrants. "An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials." Environmental Engineering Science (2002).

Maryland Department of Health. "Fact Sheet-Coal Fly Ash and Its Health Risks." 2007.

Slavin, W. *Analytical Chemistry*. Vol. 54. 1982.

U. S. Environmental Protection Agency. "Consumer Factsheet on Thallium." *National Primary Drinking Water Regulations*. n.d.

U.S. E.P.A. *Drinking Water Contaminants*. 21 September 2010. 26 10 2010. <http://water.epa.gov/drink/contaminants/index.cfm>.

US EPA. "Toxicity Characteristic Leaching Protocol." July 1992.

Wolfe, William, et al. *FGD By-Product Utilization at Ohio Coal Mine Sites: Past, Present, & Future*. Columbus, 2010.

Appendix A: Calibration Data

Calibration Standards & Curve

Table B-1: Calibration Data

Sample	Absorbance	Concentration
STANDARD 0	0.0009	0
STANDARD 1	0.0254	3.75
STANDARD 2	0.0476	7.5
STANDARD 3	0.1191	18.75
STANDARD 4	0.3001	56.25
STANDARD 5	0.389	75
reslope		7.5

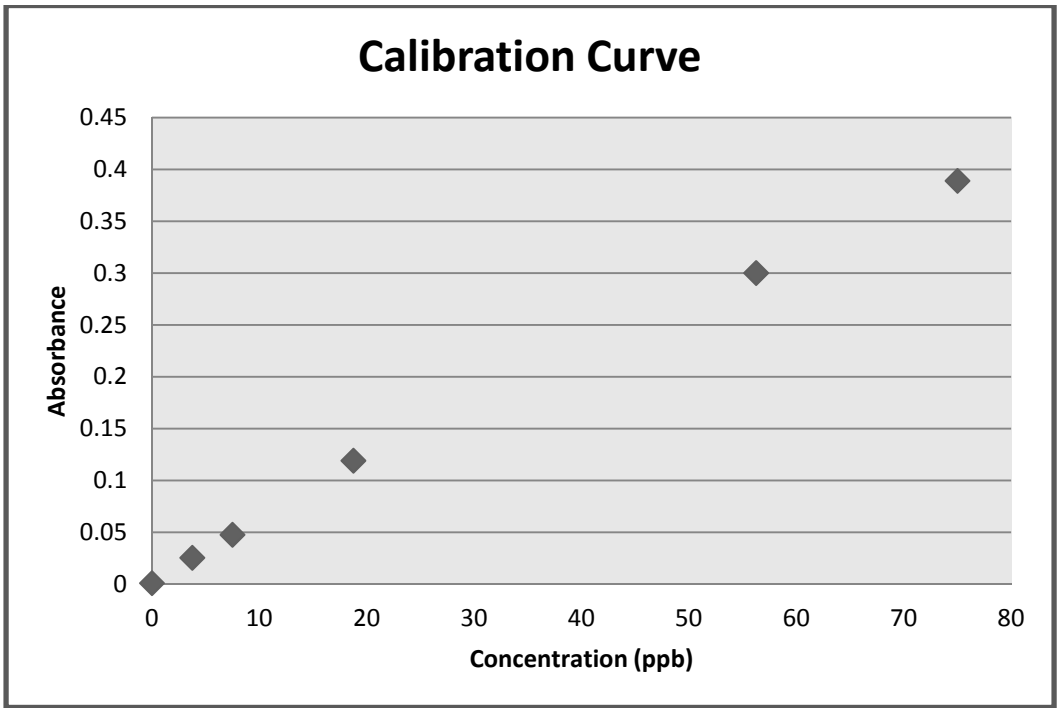

Figure B-1: Calibration Curve for final GFAAS data collection

Appendix B: Total Thallium Analysis Data

Raw Data with Quality Control Checks

Table C-1: Raw data from the final total thallium GFAAS analysis

Sample ID	Label	Total Thallium (ppb)
1:01	QC 25ppb	24.835
1:02	Blank	0.494
1:03	40 ml NaOH (1)	11.1
1:04	40 ml NaOH (2)	4.328
1:05	40 ml NaOH (3)	3.871
1:06	blank	0.111
1:07	30 ml NaOH (1)	3.829
1:08	30 ml NaOH (2)	3.09
1:09	30 ml NaOH (3)	2.901
1:10	QC 25 ppb	23.79
1:11	blank	0.007
1:12	20 ml NaOH (1)	1.451
1:13	20 ml NaOH (2)	3.051
1:14	20 ml NaOH (3)	1.641
1:15	Blank	0.029
1:16	10 ml HNO3 (2)	113.012
1:17	10 ml HNO3 (3)	127.252
1:18	QC 25ppb	29.142
1:19	blank	0.817
1:20	LS 20 (1)	36.127
1:21	LS 20 (2)	34.853
1:22	LS 20 (3)	35.914
1:23	blank	0.394
1:24	LS 10 (1)	51.517
1:25	LS 10 (2)	39.489
1:26	LS 10 (3)	36.648
1:27	QC 25 ppb	25.51
1:28	blank	0.149
1:29	LS 16 (1)	44.792
1:30	LS 16 (2)	36.318
1:31	LS 16 (3)	28.918
1:32	blank	0.048
1:33	LS 5 (1)	70.826
1:34	LS 5 (2)	57.509
1:35	LS 5 (3)	71.005
1:36	QC 25 ppb	27.492
1:37	blank	0.06
1:38	LS 2 (1)	78.677
1:39	LS 2 (2)	81.882
1:40	LS 2 (3)	117.608
1:41	blank	1.146
1:42	LS 1 (1)	56.359
1:43	LS 1 (2)	45.459
1:44	LS 1 (3)	46.337
1:45	QC 25 ppb	25.32
1:46	blank	0.772
1:47	method blank 1	0.223
1:48	method blank 2	0.163
1:49	TCLP blank	0.475
1:50	filter blank	0.064

Metadata from Final Analysis

Table C-2: Measures of Data Quality

Sample ID	Label	Total Thallium (ppb)	% Error of Standards	Average Measurement	Std Deviation
1:01	QC 25ppb	24.835	0.66		
1:02	Blank	0.494			
1:03	40 ml NaOH (1)	11.1		6.433	4.0481
1:04	40 ml NaOH (2)	4.328			
1:05	40 ml NaOH (3)	3.871			
1:06	blank	0.111			
1:07	30 ml NaOH (1)	3.829		3.27333	0.4904
1:08	30 ml NaOH (2)	3.09			
1:09	30 ml NaOH (3)	2.901			
1:10	QC 25 ppb	23.79	4.84		
1:11	blank	0.007			
1:12	20 ml NaOH (1)	1.451		2.0477	0.8740
1:13	20 ml NaOH (2)	3.051			
1:14	20 ml NaOH (3)	1.641			
1:15	Blank	0.029			
1:16	10 ml HNO3 (2)	113.012		120.132	10.069
1:17	10 ml HNO3 (3)	127.252			
1:18	QC 25ppb	29.142	16.568		
1:19	blank	0.817			
1:20	LS 20 (1)	36.127		35.6313	0.6824
1:21	LS 20 (2)	34.853			
1:22	LS 20 (3)	35.914			
1:23	blank	0.394			
1:24	LS 10 (1)	51.517		42.5513	7.8933
1:25	LS 10 (2)	39.489			
1:26	LS 10 (3)	36.648			
1:27	QC 25 ppb	25.51	2.04		
1:28	blank	0.149			
1:29	LS 16 (1)	44.792		36.676	7.9431
1:30	LS 16 (2)	36.318			
1:31	LS 16 (3)	28.918			
1:32	blank	0.048			
1:33	LS 5 (1)	70.826		66.4467	7.7408
1:34	LS 5 (2)	57.509			
1:35	LS 5 (3)	71.005			
1:36	QC 25 ppb	27.492	9.968		
1:37	blank	0.06			
1:38	LS 2 (1)	78.677		92.7223	21.611
1:39	LS 2 (2)	81.882			
1:40	LS 2 (3)	117.608			
1:41	blank	1.146			
1:42	LS 1 (1)	56.359		49.385	6.0556
1:43	LS 1 (2)	45.459			
1:44	LS 1 (3)	46.337			
1:45	QC 25 ppb	25.32	1.28		
1:46	blank	0.772			
1:47	method blank 1	0.223		0.193	0.0424
1:48	method blank 2	0.163			
1:49	TCLP blank	0.475			
1:50	filter blank	0.064			

Compiled Data

Table C-3: Combined thallium data, source for graphs in results section

Sample ID	eq/L	fly ash (g)	Total Volume (mL)	pH	Mean pH	Std Dev (pH)	Total Tl (ppb)	Mean Thallium release/g fly ash (ug/g)	Std Dev (ug/g)	Mean Total Tl (ppb)	Std Dev (ppb)
1:03	-40	5	50	13.169	13.1960	0.0868	11.1	0.0667	0.0334	6.6705	3.3393
1:04	-40	5	50	13.308			4.328				
4/9/2012	-40	20	200	13.1			7.383				
1:05	-40	5	50	13.207			3.871				
1:07	-30	5	50	13.089	13.0558	0.0389	3.829	0.0335	0.0043	3.3528	0.4308
4/9/2012	-30	20	200	13			3.591				
1:08	-30	5	50	13.061			3.09				
1:09	-30	5	50	13.073			2.901				
1:12	-20	5	50	12.867	12.8310	0.1219	1.451	0.0231	0.0089	2.3123	0.8885
4/9/2012		20	200	12.65			3.106				
1:13	-20	5	50	12.903			3.051				
1:14	-20	5	50	12.904			1.641				
1:24	0	5	50	7.802	8.0390	0.2107	51.517	0.4160	0.0672	41.6030	6.7182
4/9/2012		20	200	8.11			38.758				
1:25	0	5	50	8.205			39.489				
1:26	0	5	50	--			36.648				
1:16	20	5	50	1.706	1.6637	0.0490	113.012	1.1822	0.0785	118.2177	7.8542
4/9/2012	20	20	200	1.61			114.389				
1:17	20	5	50	1.675			127.252				
1:20	20	2.5	50	8.198	8.1413	0.0491	36.127	0.7126	0.0136	35.6313	0.6824
1:21	20	2.5	50	8.115			34.853				
1:22	20	2.5	50	8.111			35.914				
1:29	16	3.125	50	7.898	8.0853	0.2216	44.792	0.5868	0.1271	36.6760	7.9431
1:30	16	3.125	50	8.028			36.318				
1:31	16	3.125	50	8.33			28.918				
1:24	10	5	50	7.802	8.0390	0.2107	51.517	0.4160	0.0672	41.6030	6.7182
1:25	10	5	50	8.205			39.489				
4/9/2012	10	20	200	8.11			38.758				
1:26	10	5	50	--			36.648				
1:33	5	10	50	7.905	7.9690	0.1048	70.826	0.3322	0.0387	66.4467	7.7408
1:34	5	10	50	8.09			57.509				
1:35	5	10	50	7.912			71.005				
1:38	2	12.5	25	7.942	8.0757	0.1293	78.677	0.1854	0.0432	92.7223	21.6111
1:39	2	12.5	25	8.2			81.882				
1:40	2	12.5	25	8.085			117.608				
1:42	1	25	25	8.104	8.1830	0.0737	56.359	0.0494	0.0061	49.3850	6.0556
1:43	1	25	25	8.195			45.459				
1:44	1	25	25	8.25			46.337				